NASA/TM—1999-209292

# Heat Treatment Effects on Microstructure of SiC Fiber Preforms

Ramakrishna T. Bhatt
U.S. Army Research Laboratory, Glenn Research Center, Cleveland, Ohio

Yuan L. Chen
Dynacs Engineering Company Inc., Cleveland, Ohio



July 1999

## The NASA STI Program Office . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.

- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.

- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized data bases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at ***http://www.sti.nasa.gov***

- E-mail your question via the Internet to help@sti.nasa.gov

- Fax your question to the NASA Access Help Desk at (301) 621-0134

- Telephone the NASA Access Help Desk at (301) 621-0390

- Write to:
  NASA Access Help Desk
  NASA Center for AeroSpace Information
  7121 Standard Drive
  Hanover, MD 21076

NASA/TM—1999-209292

# Heat Treatment Effects on Microstructure of SiC Fiber Preforms

Ramakrishna T. Bhatt
U.S. Army Research Laboratory, Glenn Research Center, Cleveland, Ohio

Yuan L. Chen
Dynacs Engineering Company Inc., Cleveland, Ohio

Prepared for the
101st Annual Conference
sponsored by the American Ceramic Society
Indianapolis, Indiana, April 25–28, 1999

National Aeronautics and
Space Administration

Glenn Research Center

July 1999

Trade names or manufacturers' names are used in this report for identification only. This usage does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076
Price Code: A03

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100
Price Code: A03

# HEAT TREATMENT EFFECTS ON MICROSTRUCTURE OF SiC FIBER PREFORMS

Ramakrishna T. Bhatt
U.S. Army Research Laboratory
NASA Glenn Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
and
Yuan L. Chen
Dynacs Engineering Company, Inc.
NASA Glenn Research Center
21000 Brookpark Road
Cleveland, Ohio 44135

## ABSTRACT

Preforms of BN/SiC coated Sylramic SiC fibers were heat treated at $1420^0$, $1600^0$, and $1800^0$C in 0.1 MPa argon or at $1800^0$C in 103 MPa nitrogen for 1h. Optical, SEM, and TEM techniques were used to analyze the effects of environmental exposure on constituent microstructure of the preforms. TEM analysis of the as-received preforms indicates that the CVI BN coating is predominantly amorphous with small amounts of microcrystalline BN grains, and that the SiC coating on top of the BN coating and SiC fibers is polycrystalline. With increasing temperature of exposure from $1420^0$ to $1800^0$C, the preforms heat treated in argon showed increasing amounts of crystalline BN in the CVI BN coating, and coarsening of SiC grains in the CVI SiC coating and SiC fibers. On the other hand, the preforms heat treated in 103 MPa nitrogen at $1800^0$C for 1h showed microstructural changes inside the fiber tows similar to those heat treated at $1800^0$C in 0.1 MPa argon for 1h, but the same preforms on the outer periphery of the tows showed reaction between nitrogen and the CVI SiC coating to form $Si_3N_4$.

KEYWORDS: SiC fibers, Preform, Microstructure, Environmental effects, BN/SiC interface.

## INTRODUCTION

Preforms of boron nitride/silicon carbide (BN/SiC) coated Sylramic SiC fibers are being used as a starting assembly for the fabrication of SiC/SiC composites. The preforms are fabricated by stacking 2-D woven mats of SiC fibers in a fixture and then infiltrating the fixture with BN and SiC coatings by chemical vapor infiltration (CVI). A variety of processes are used for further densification including CVI, polymer infiltration and pyrolysis, and melt infiltration (MI). For melt infiltration, the fiber preforms are infiltrated with SiC particle slurry and then with molten silicon metal to fabricate SiC/SiC composites [1]. Damage to the fibers and interface coating during preform fabrication is minimum when compared with other consolidation processes that involve pressure. Complex shaped preforms can be easily manufactured by CVI process. The SiC/SiC composites fabricated by the MI approach show adequate performance potential and properties required for the next generation turbine components, but are limited to $1200^0$C applications because of the presence of high amounts of residual silicon (10-20 vol%) in the SiC matrix [1]. Although residual silicon is known to improve properties of SiC/SiC composites such as, thermal conductivity, it is an undesirable constituent in rotating components because it reduces stiffness of the components above $1200^0$C and it sweats out from components operating at temperatures > $1420^0$C and reacts with surrounding metallic attachments. To develop SiC/SiC composites stable to $1400^0$C, a variety of processing approaches, which do not involve MI infiltration of silicon, are being explored. Some of these approaches include infiltration of the preforms with silicon alloys or silicides, which melt at least 100 to $200^0$C above the operating temperature of the component. In these cases, the preforms are exposed to temperatures ranging from $1420^0$ to $1800^0$C in argon or in nitrogen. However, the microstructural and strength stabilities of the preforms under these conditions are not fully understood. In this paper, the microstructural stability of the preforms under silicide melt infiltration conditions is investigated.

## EXPERIMENTAL

The BN/SiC coated Sylramic SiC fiber preforms were purchased from AlliedSignal Composites, Newark, Delaware. Sylramic is the trade name of SiC fiber manufactured by The Dow Corning Company, Midland, Michigan. For conciseness henceforth this preform will be referred to as Sylramic preform. The preforms are prepared by stacking eight layers of 2-D woven 5-harness-satin (5HS) SiC fiber mats (152 mm x 229 mm) and then infiltrating the assembly with the BN and SiC coatings by a proprietary CVI process. Typical dimensions of the as-processed preforms were 152 mm x 229 mm x 2 mm. The preforms consist of ~40 vol. % SiC fiber, ~3-8 vol. % BN, ~18-30 vol. % SiC, and ~20-40 vol. % open porosity. Rectangular specimens of dimensions 152mm x 13mm x 2mm

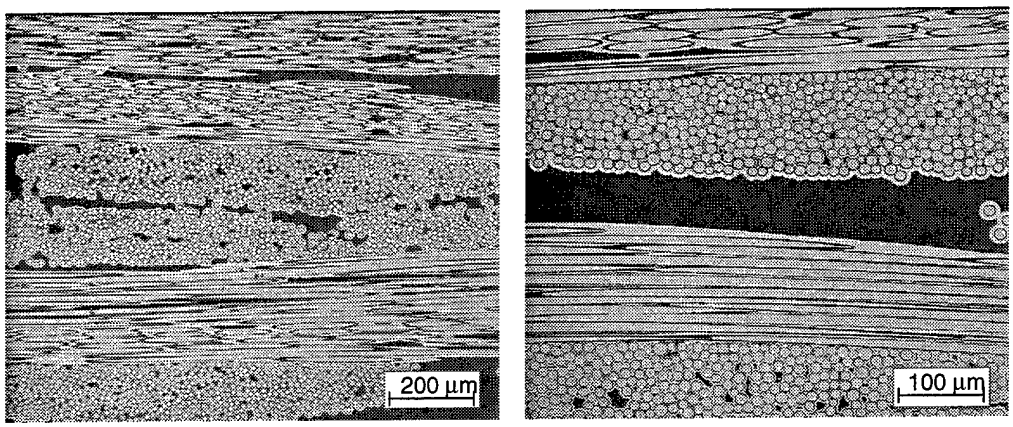
were cut from the larger preforms using a diamond impregnated metal bonded cut-off wheel. The specimens were heat-treated in a box furnace at $1420^0$, $1600^0$, and $1800^0$C in 0.1 MPa argon for 1h or in a hot isostatic press at $1800^0$C in 103 MPa nitrogen for 1 h.

For the preparation of transmission electron microscope (TEM) specimens, the preform specimens were sliced using a diamond saw. Each piece was sandwiched between two sacrificial silicon wafers. The assembly was vacuum degassed and infiltrated with epoxy. After curing the sandwich assembly was sectioned to a size of 2.5mm x 2mm x 0.5mm. After polishing one side, the second side of the specimen was thinned to electron transparency using a tripod polishing method typically used for polishing silicon chips in the electronic industry [2]. As polishing progresses, the thickness of the assembly was determined from the color of sacrificial silicon. Tripod polishing allows one to mechanically polish a large area of the specimen to electron transparency with no or minimal mechanical damage to the specimen. Any mechanical damage occurring to the specimen can be removed by argon ion milling at a low angle (less than 7 degrees) for about 10 to 20 minutes. Diffraction contrast and phase contrast images, selected area diffraction (SAD) data were recorded using a Philips CM200 electron microscope operated at 200 kV. The TEM is coupled to an energy dispersive x-ray (EDX) spectrometer for chemical identification. The present TEM results include analyses from cross-sectional preforms. In this mode, the fibers were observed 'end-on'.

## RESULTS

The optical micrographs of a typical cross-section of a BN/SiC coated Sylramic SiC preform are shown in Fig. 1. In this figure, the dark ring around the fibers is the BN coating and the light gray region on top of the BN coating is the SiC coating. The SiC coating thickness varies from tow to tow as well from the middle to the periphery of the tow. The tows contain ~10 μm diameter fibers. The fiber tows appeared to be sealed off during early stages of SiC coating thus preventing greater amounts of SiC deposition in the interior of the tows. As a result a thick SiC layer is noticed in figure 1(b).

A low magnification TEM diffraction contrast image of a tripod polished Sylramic fiber preform specimen is shown in figure 2. The advantages of the tripod polishing technique are quite obvious. With conventional TEM specimen preparation techniques, ~ $20\mu m^2$ of electron transparent area can be examined, whereas with the tripod technique ~ 800 $\mu m^2$ of electron transparent area can be examined routinely. The larger electron transparent area also helps in generating statistically reliable chemical analysis averaged over several fibers and interfaces.




(a) (b)

Fig. 1 Optical photographs of the cross-section of BN/SiC coated Sylramic SiC preforms showing fiber distribution and CVI SiC coating thickness variation.

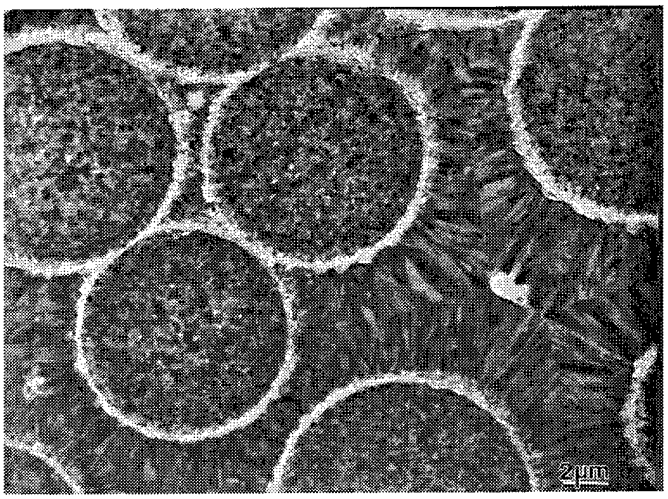



Fig. 2 TEM micrograph of a preform specimen prepared by the tripod polishing method showing electron transparent region.

TEM micrographs and selected area diffraction (SAD) pictures of the as-fabricated Sylramic preforms are shown in Fig. 3. Results indicate that the BN interface is mostly amorphous, and the CVI SiC coating is poly-crystalline. The grains in the CVI SiC coating are columnar and grow radially. The boundary between the SiC fiber and BN coating or between the BN and SiC coatings is sharp and distinct, indicating no reaction between coatings or between the SiC fiber and BN coating. However in a few cases a graded zone of fine grained SiC and amorphous BN is noticed at the BN/SiC interface. The SiC fiber contains randomly oriented SiC grains of ~100 nm nominal diameter. The EDX analysis shows small amounts Si, C, O impurities in the BN coating and the presence of Ti and B impurities in the SiC fiber. High resolution TEM of the fiber confirms the presence of $TiB_2$ particles at the triple junction of the SiC grains. This result is in agreement with analyses of Sylramic fibers by Lipowitz et al [3 ].

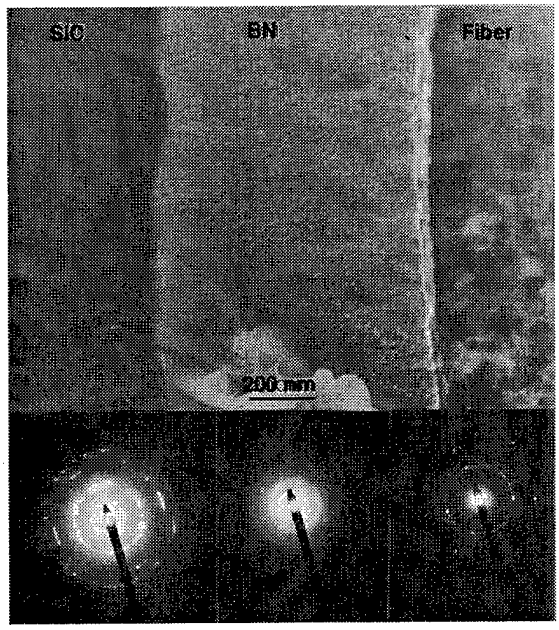



Fig. 3 TEM micrographs of the interface zone of as-received BN/SiC coated Sylramic SiC preforms.

A TEM micrograph of a section from the preform heat-treated in argon at $1420^0$C for 1h is shown in Fig. 4. This temperature was chosen because at this temperature silicon melts. The influence of heat treatment temperature on constituent microstructure can be recognized when Fig. 4 is compared with Fig. 3. The BN coating shows growth of a randomly oriented whisker-like structure, and

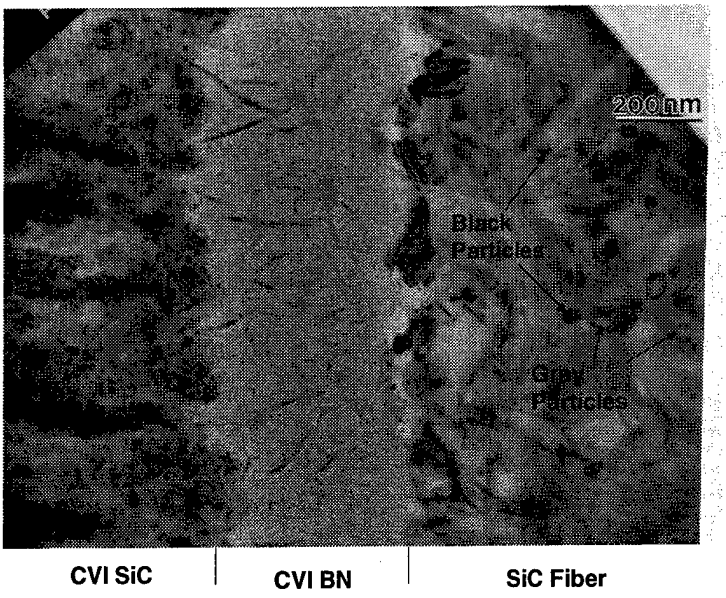



Fig. 4 TEM micrograph of the cross-section of BN/SiC coated Sylramic preform heat treated in 0.1 MPa argon at 1420$^0$C for 1h.

the CVI SiC coating shows slight coarsening of the SiC grains. The SiC fiber contains gray and black particles. The boundary between the SiC fiber and the BN interface coating is jagged and wavy. The EDX analysis shows reduced oxygen content in the BN coating when compared with that of the BN coating in the as-received preform. The spot analysis indicates that the gray particles are composed of Ti and B, and the black particles are rich in Si, B, and C.

Figure 5 is the TEM micrograph of a section from the preform heat-treated in argon at 1800$^0$C for 1h. Figure 5 shows rod-like structures in the BN coating and coarsening of SiC grains in the CVI SiC coating. The SiC grain size almost doubled compared to that of the as-received fiber. In addition, the Ti-rich particles coarsened and migrated from the interior to the outer surface of the fiber. The boundary between the BN coating and SiC fiber or between the BN coating and CVI SiC coating is not as distinct indicating inter diffusion between the species.

Figure 6 is the high-resolution TEM micrograph and SAD pattern of a rod-like structure seen in the BN coating of Fig. 4. The alignment of diffraction spots in a row suggests that this region is crystalline and composed of a layered structure. The distance between the fringes in Fig. 6 corresponds to a d spacing between the lattice planes of the crystal. The measured d spacing is ~ 0.33 nm which compares well with the d spacing value of the [002] lattice plane of $\alpha$-BN reported in the literature [4 ].

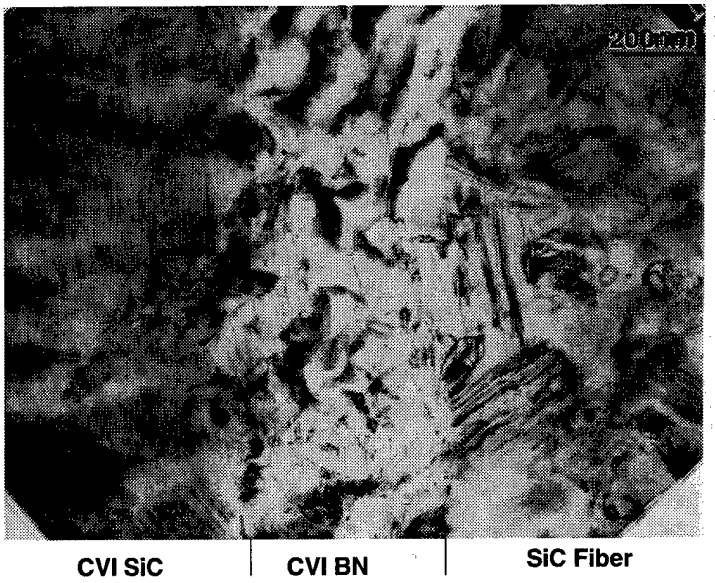



Fig. 5 TEM micrograph of the cross-section of BN/SiC coated Sylramic preform heat treated in 0.1 MPa argon at $1800^0$C for 1h.

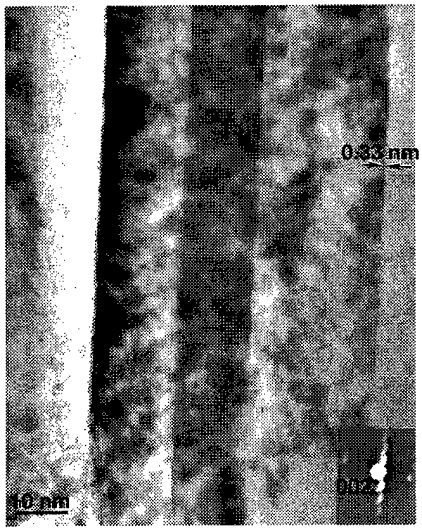


Fig. 6 High resolution lattice image and SAD pattern of a rod-like structure in the CVI BN coating after $1800^0$C 1h heat treatment in 0.1 MPa argon.

Figure 7 is the TEM micrograph of a gray particle in the SiC fibers as shown in Figs. 4 and 5. The EDX analysis indicates that the particle is composed of Ti and B. Based on EDX and SAD information, this particle is identified as $TiB_2$.

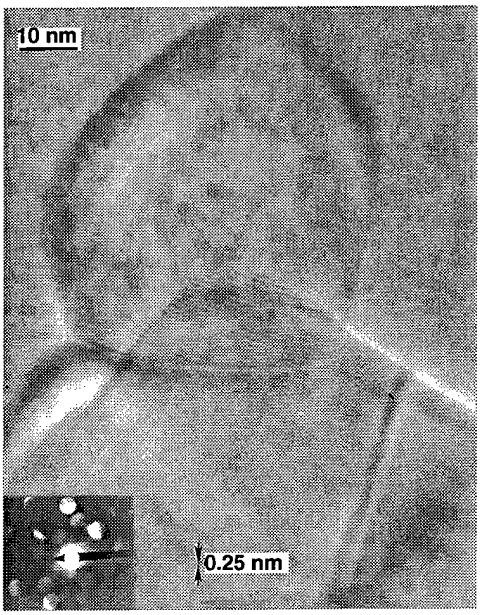



Fig. 7 TEM image and SAD pattern of the $TiB_2$ particles in SiC fibers of BN/SiC coated Sylramic preforms heat treated in 0.1 MPa argon for 1h at $1800^0$C.

Figure 8 is the TEM micrograph of the cross-section of BN/SiC coated Sylramic preforms heat-treated in 103 MPa nitrogen at $1800^0$C for 1h. This section represents an area near the center of the fiber tow. Figure 8 shows coarsening of SiC grains in the SiC fiber and CVI SiC coating, and crystallization of amorphous BN similar to that observed in Fig. 5. On the other hand, examination of the outer periphery of the tows of the nitrogen treated preform indicates void formation up to a distance of ~1μm from the surface of the CVI SiC coating (Fig. 9). The elemental x-ray line profile across this region shows predominantly nitrogen and silicon indicating formation of $Si_3N_4$ (Fig. 10). Based on this observation, we concluded that heat treatment of preforms in 103 MPa nitrogen at $1800^0$C for 1h causes partial conversion of CVI SiC coating to $Si_3N_4$.

In conclusion, the results of this study indicate Sylramic preforms are not stable microstructurally when heat-treated in argon or in nitrogen environment

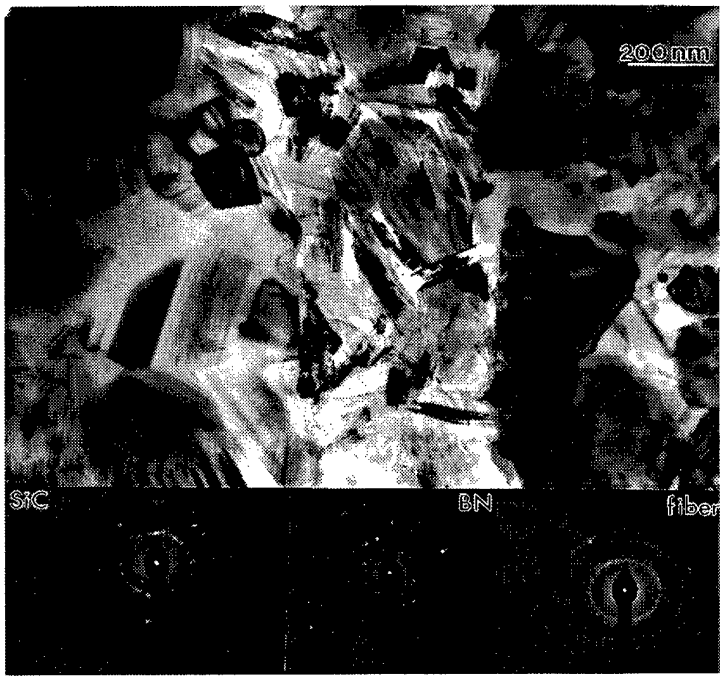



Fig. 8 TEM micrograph of the cross-section of BN/SiC coated Sylramic SiC fiber preform heat treated in 103 MPa nitrogen at 1800$^0$C for 1h.

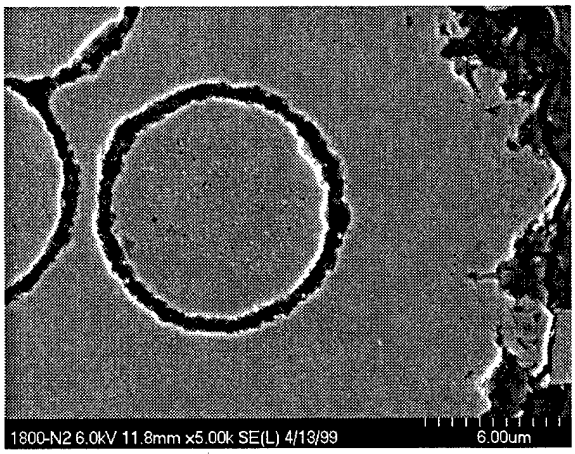



Fig. 9 SEM micrograph of the cross-section of BN/SiC coated Sylramic preform heat treated in 103 MPa nitrogen at 1800$^0$C for 1h showing voids near the surface of CVI SiC coating.

between 1420 and 1800$^0$C for 1h. However, the effect of microstructural changes on the strength properties must also be studied to determine the suitability of using these preforms for melt infiltration at temperatures greater than 1420$^0$C.

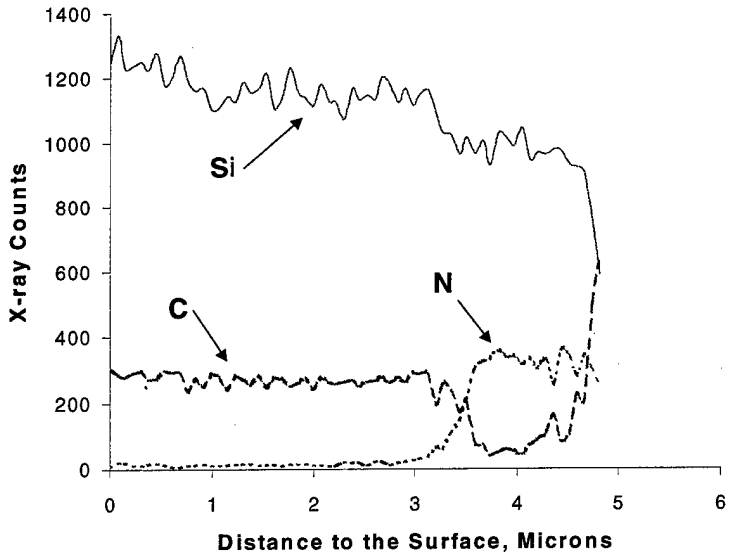



Fig. 10 EDX/SEM line profile of across the CVI SiC coating of the BN/SiC coated Sylramic SiC fiber preform heat treated in 103 MPa nitrogen at 1800$^0$C for 1h showing formation of $Si_3N_4$.

## SUMMARY OF RESULTS

The effects of temperature and environment on microstructural stability of BN/SiC coated Sylramic preforms were analyzed by optical microscopy, SEM, TEM, and EDX, and the results are as follow.

1. In 1 hr argon treatment, the amount of crystalline BN in the BN the coating, the grain size of SiC grains in the CVI SiC coating and SiC fibers, and coarsening and migration of $TiB_2$ particles from the interior to the surface of the SiC fibers increased with increasing temperature from 1420 to 1800$^0$C.
2. In the interior region of the tows, Sylramic preforms heat treated at 1800$^0$C in 103 MPa nitrogen for 1h showed microstructural changes similar to those heat treated at the same temperature in argon, but on the outer periphery of the tows, the preforms showed reaction between the CVI SiC coating and nitrogen to form $Si_3N_4$.

## REFERENCES

[1] A. M. Johnson, B. J. Bartlett, and W. A. Troha, "Material Challenges and Progress Toward Meeting the High Speed Civil Transport Propulsion Design Requirements," *Proceedings of the 13th International Symposium on Air Breathing Engines*, Chattanooga, Tennessee, U.S.A., September 7-12, 1997, Vol. II, ISABE 97-7179, Edited by S. Billing, pp. 1321-1328.

[2] J. P. Benedict, S. J. Klepeis, and R. Anderson, "The Development and Application of the Tripod Polishing Technique in Microscopy and Microanalysis," **3**, (2), Proceedings: Microscopy and Microanalysis, Cleveland, Ohio, Aug 10-14, 1997, New York; Springer-Verlag, New York Inc., pp. 339-340.

[3] J. Lipowitz, J. A. Rabe, A. Zangvil, and Y. Xu, "Structure and Properties of Sylramic™ Silicon Carbide Fiber-A Polycrystalline, Stoichiometric–SiC Composition," *Ceramic Engineering and Science Proceedings,* **18**, 147 (1997).

[4] A. Lipp, K. A. Schwetz, and K. Hunold, "Hexagonal Boron Nitride: Fabrication, Properties and Applications," *J. Eur. Ceram. Soc.*, **5**, 3-9 (1989).

# REPORT DOCUMENTATION PAGE

*Form Approved*
*OMB No. 0704-0188*



| 1. AGENCY USE ONLY (*Leave blank*) | 2. REPORT DATE | 3. REPORT TYPE AND DATES COVERED |
|---|---|---|
| | July 1999 | Technical Memorandum |

**4. TITLE AND SUBTITLE**

Heat Treatment Effects on Microstructure of SiC Fiber Preforms

**5. FUNDING NUMBERS**

WU–523–21–13–00

**6. AUTHOR(S)**

Ramakrishna T. Bhatt and Yuan L. Chen

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

National Aeronautics and Space Administration
John H. Glenn Research Center at Lewis Field
Cleveland, Ohio 44135–3191

**8. PERFORMING ORGANIZATION REPORT NUMBER**

E–11766

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

National Aeronautics and Space Administration
Washington, DC 20546–0001

**10. SPONSORING/MONITORING AGENCY REPORT NUMBER**

NASA TM—1999-209292

**11. SUPPLEMENTARY NOTES**

Prepared for the 101st Annual Conference sponsored by the American Ceramic Society, Indianapolis, Indiana, April 25–28, 1999. Ramakrishna T. Bhatt, U.S. Army Research Laboratory, NASA Glenn Research Center; Yuan L. Chen, Dynacs Engineering Company Inc., Cleveland, Ohio. Responsible person, Ramakrishna T. Bhatt, organization code 0300, (216) 433–5513.

**12a. DISTRIBUTION/AVAILABILITY STATEMENT**

Unclassified - Unlimited
Subject Category: 27 Distribution: Nonstandard

This publication is available from the NASA Center for AeroSpace Information, (301) 621–0390.

**12b. DISTRIBUTION CODE**

**13. ABSTRACT** (*Maximum 200 words*)

Preforms of BN/SiC coated Sylramic SiC fibers were heat treated at 1420°, 1600°, and 1800 °C in 0.1 MPa argon or at 1800 °C in 103 MPa nitrogen for 1 h. Optical, SEM, and TEM techniques were used to analyze the effects of environmental exposure on constituent microstructure of the preforms. TEM analysis of the as-received preforms indicates that the CVI BN coating is predominantly amorphous with small amounts of microcrystalline BN grains, and that the SiC coating on top of the BN coating and SiC fibers is polycrystalline. With increasing temperature of exposure from 1420° to 1800 °C, the preforms heat treated in argon showed increasing amounts of crystalline BN in the CVI BN coating, and coarsening of SiC grains in the CVI SiC coating and SiC fibers. On the other hand, the preforms heat treated in 103 MPa nitrogen at 1800 °C for 1 h showed microstructural changes inside the fiber tows similar to those heat treated at 1800 °C in 0.1 MPa argon for 1 h, but the same preforms on the outer periphery of the tows showed reaction between nitrogen and the CVI SiC coating to form $Si_3N_4$.

**14. SUBJECT TERMS**

SiC fibers; Preform; Microstructure; Environmental effects; BN coating; TEM; SEM

**15. NUMBER OF PAGES**
17

**16. PRICE CODE**
A03

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| Unclassified | Unclassified | Unclassified | |